LA-UR-18-22217

Title:	Smart Polymer Gels as Sealants for Wells
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Intended for:	Report
Issued:	2018-03-15

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March 19, 2018

Smart Polymer Gels as Sealants for Wells

Abstract

Exploitation of natural resources via a well requires increasing lifetimes of those wells to become economically viable. Environmental and personnel safety is paramount. Development of new methods, procedures, and maintenance ensuring these wells remain safe throughout their lifetimes is vital. Small void spaces (microannuli) in the casings, cement barriers, and sandscreens of the well must be sealed to prevent harmful leaks and further degradation of the structure.[1] A recent patent mitigates these problems by sealing voids with a swellable cross-linked polymer gel that can be triggered via pH, temperature, concentration of metal ions, and/or acoustic, electric, and/or magnetic stimuli.[1] Currently, these gels are reversible, but future studies will focus on a more permanent triggerable sealant.

<u>Introduction</u>

The extraction of natural gas and oil is an increasingly complex and expensive process. Fewer wells must produce longer to justify costs and reach economic viability. New methods, systems, and controls must be implemented to ensure environmental safety, improvements and maintenance in wells.[1]

A wellbore (Figure 1) is constructed of series of metal casings with cement reinforcement. There can be several layers of casings and cement. Centrally there may be a void where drilling fluid or drilling mud circulates to aid in the drilling process. Over time, due to earth composition or stresses induced by drilling, microannuli, here defined as any void less than 120 microns, can form either in the casings or in the cement. There may also be voids in the sandscreen, due to stresses from drilling or packing in the initial stages. These voids allow oil, drilling fluid, harmful gases, etc. to migrate out into the surrounding environment, causing environmental damage as well as safety concerns. Migration through these voids can also result in structural damage to the wellbore, causing more microannuli or worsening voids that already exist. Due to gases migrating through the voids, pressure can build leading to structural damage that could, in the worst cases, result in the failure of the well.[1]
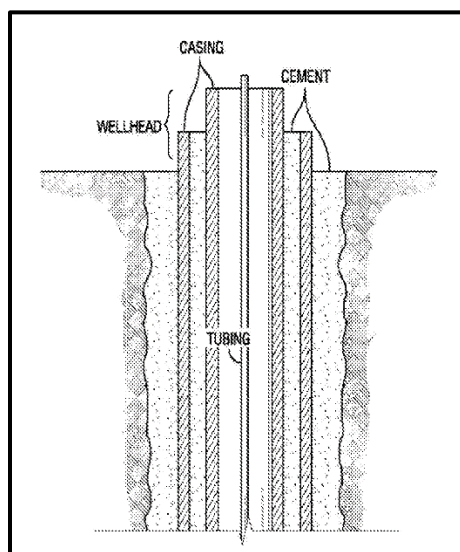

Figure 1: General image of a wellbore showing the casing and cement barriers.[1]

Replacing components is time consuming, expensive, and in some cases impossible. This paper will focus on the use and implementation of polymer hydrogels as sealants.

Hydrogels, either synthetic or naturally occurring, are lightly cross-linked polymers that can expand their structure as a response to a stimulus by the uptake of fluid (Figure 2).[2] Hydrogel expansion is triggered by an external stimulus that can be controlled and manipulated based on the application. The ability of these polymers to respond to a stimulus gives them the name, smart gels.[2] Hydrogels have been extensively studied and reported on in literature, with much of the research focusing on pH and temperature responsive materials.[2-4] Research has also been centered on biomedical applications, particularly drug delivery due to hydrogels high water content and biocompatibility.[3] Hydrogels have been used for drilling applications and most of the work is in the form of patents. The ability to be triggered on and off as well as the expansion of the gels makes them particularly attractive for drilling applications, as they can be

prepared to a size that can fit into a void and then at a particular time can be triggered to swell to fill that void.[1]
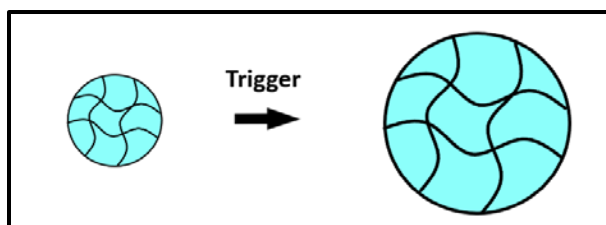

Figure 2: On the left is cross-linked gel particle in the collapsed state, introduction of a trigger causes the gel to swell in size, to the expanded state.

The main factors to consider when designing a polymer hydrogel include the chemical backbone and crosslinking. A hydrogel swells when the polymer backbone responds to a stimulus with a positive or negative expansion in free volume and uptakes fluid.[2] One example that is heavily studied is pH responsive hydrogels; in these hydrogels weak acids or bases are incorporated along the backbone and will ionize (Figure 3). Ionizing will lead to a charge along the backbone, the charges will electrostatically repel each other causing the gel to expand its free volume and the polar molecules will interact with the charged moieties in the gel, causing the gel to uptake water and swell.[2,5] Hydrogels can be triggered with small changes in pH; a weakly acidic backbone will expand when the environment is above its dissociation constant at higher pH's. While a weakly basic backbone will expand at lower pH's.[2,5] Therefore, the ability to ionize is a requirement of the polymer backbone, for pH sensitive hydrogels. For this reason acrylic acid and other acrylates are often chosen for pH responsive applications. Naturally occurring polymers such as alginate, chitin, and cellulose can also be used in pH responsive applications as they exhibit this ionizing behavior.[2]

Other stimuli, such as temperature, may also affect swelling in hydrogels. Slight changes in temperature can change how much the gel swells. N-isopropylacrylamide (NiPAM) exhibits a lower critical solution temperature LCST of around 32°C.[6-9] NiPAM will swell below its LCST and will collapse above the LCST. Other polymers, exhibiting an upper critical solution temperature (UCST), will expand above their UCST and collapse below it.[9] Ionic charge of the polymer again plays a vital role in determining temperature swelling behavior. Increasing the charge in a polymer network increases hydrophilicity, decreases the hydrophobicity, and allows more hydrogen bonding interactions with water.[9] When NiPAM is below its LCST hydrogen bonding between hydrophilic groups and water are able to form a cage structure around any hydrophobic groups, mitigating the hydrophobic effect.[6-9] Temperatures above the LCST interrupt hydrogen bonding; hydrophobic interactions become more dominant, this leads to an entropic induced collapse in volume.[6-9]

Hydrogels can take advantage of more than one trigger by incorporating multiple monomers sensitive to differing stimuli into the backbone. Meaning a hydrogel may be sensitive to pH and temperature changes.[9]
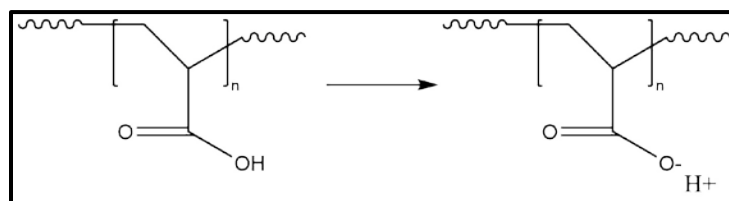
Figure 3: A general case of Poly(acrylic acid) disassociating, the negative charge will cause repulsion in the molecule; therefore the molecule will expand.

One might expect that a gel with such high free volume and high fluid content would be unstable and not durable, this, however, is not the case. Hydrogels can have well defined strong structures due to the crosslinking in the material. The degree to which the system is cross-linked can be tuned to enhance the swelling, strength and other properties of the hydrogel depending upon the application. There are four types of crosslinking that occur; physical entanglement, covalent crosslinks, ionic crosslinks, and the formation of an interpenetrating polymer network (IPN), shown in Figure 4.[2] Physical entanglements occur when a number of the polymer chains intertwine and interact to form a network. A physical process can undo a physical crosslink. Covalent crosslinks results when a chemical reaction has been used to covalently link chains together in a network.[2,10] Ionic crosslinks arise from positive and negative charges along the backbone that interact and hold the hydrogel together in a network. An IPN is two or more polymer networks interlaced but not covalently linked.[2,10,11] This differs from physical crosslinks, in an IPN chemical bonds must be broken to separate the network. A polymer gel may use a combination of these to impart strength in the system.
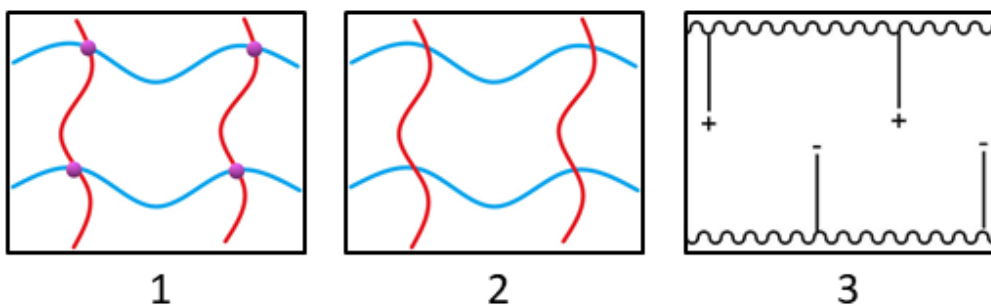
Figure 4: (1) represents a chemical crosslink, the chains are bonded at the overlapping points, (2) represents a physical crosslink, the chains are entangled but not chemically linked, (3) represents ionic interactions between chains.

The density of these crosslinks is a large factor that affects the overall properties of the hydrogel. Greater density will reduce the capacity to swell while less density will increase capacity. Greater crosslink density increases the mechanical properties of the hydrogel, imparting durability. However, there is an optimal crosslink density for hydrogels, too much crosslinking will lead to a brittle hydrogel lacking in durability. Although crosslinking imparts many useful properties to a gel, it also presents drawbacks; mainly that crosslink density may not be homogenously distributed throughout the gel. This leads to decreases in

optical clarity and strength. As mentioned above, the degree to which a gel can interact and crosslink can be tailored synthetically.[2]

Most of the work done in hydrogels as sealants is kept in patents, mostly held by energy companies, such as Haliburton. Recent work provides methods and implementation of gels as well as varying compositions and methods for crosslinking as solutions to sealing voids in wellbores.

<u>Current Art</u>

Current developments address the problem of voids within wellbores. A void being any area in the well where there is no solid, only liquid or gas. In a recent patent, a series of triggerable swellable gel sealants were created that swell in response to various stimuli. These sealants can be used to seal voids in the wellhead, casings, cement sheaths, sandscreens, and plugging near wellbore production zones during drilling, completion, production, and plugging of wells. This patent describes a method for mitigating gas leaks by monitoring a wellhead for a gas leak and injecting the triggerable gel into the well. The gel is then exposed to a trigger and will swell to a least ten times its injectable size. The patent also has a second composition that can be injected into the wellhead that can trigger swelling in the gel. The swollen gel creates a seal that will reduce or stop flow of liquid or gas through the void. The gel is reversible and flow can be restored by reversing the trigger. The hydrogel will crosslink when exposed to the trigger. The expanded gel was found to withstand any pressure from liquid or gases due to the packing and crosslinking in the individual particles. Example of a general case in Figure 5.[1]
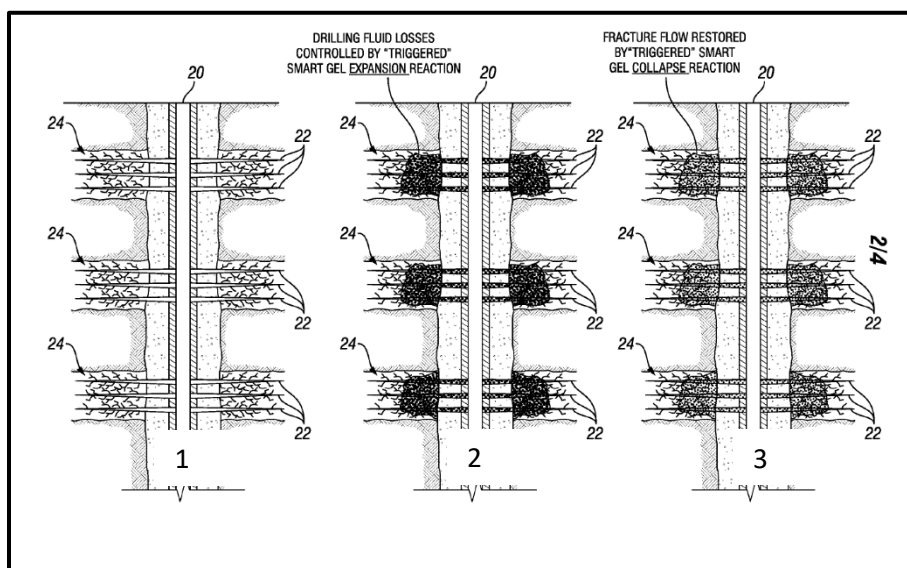
Figure 5: A general wellbore showing cracks and voids in the structure and the application of a smart gel. The numbers 20, 22, and 24 represent the wellbore, fractures, and production zones respectively. (1) The gel is not expanded, (2) the gel is expanded by a trigger, (3) finally the trigger has been removed and the gel collapses allowing flow back through the voids.[1]

The triggerable gel is made up of three essential components that comprise the backbone: inert monomer, practical monomer, and cross-linker. The cross-linker comprises less than 1.5% of the total weight. There was also a fluorescent tag added in some embodiments to aid in visualizing the swelling. The backbone of the hydrogel comprises mostly of the inert monomer, which is not triggered. The practical monomer is the component of the gel that reacts either physically and/or chemically. The cross-linker is a di-, tri-, or multi-functional monomer that will cross-link within the gel. Table 1 list all the monomers used. These components are all polymerized prior to application in the well. These are polymerized via emulsion, with the particle size controlled by the surfactant type and concentration. The size can be tailored to the application and size of void. The properties of the gel can also be tailored via the composition of the components as well as the ratios of the components.[1]

This patent claims a variety of triggers that induce swelling including: pH, temperature, concentration of metal ions, and/or acoustic, electric, and/or magnetic stimuli. Table 2 lists the practical monomers used and their respective triggers. The trigger can be introduced to the system or the gel can be triggered by internal triggers, such as temperature. In embodiments, the average size of the particles was between 10 nanometers and 100 micrometers with the size tailored to 0.05 – 0.25 times the void.[1]

Table 1: The components used to create a swellable gel.

Inert	Practical	Cross-linker
Methyl methacrylate, styrene, alkyl substituted styrenes, methyl acrylate, methacrylic and acrylic monomers, acryloyl nitrile, polyvinylpyrolidinone, substituted acrylamide	Vinyl pyridine, 2-(dimethylamino)ethyl acrylate, 2-(diethylamino)ethyl acrylate, 3-(dimethylamino)propyl acrylate, acrylic acid, N-isopropylacrylamide, Vinylimidazole or substituted versions	Ethylene glycol dimethacrylate, methylene bis-acrylamide, triethylene glycol trimethacrylate, divinyl/trivinyl-benzene

Table 2: Practical monomers used categorized by their trigger.

Trigger	Practical Monomer
pH and CO_2	Vinyl pyridine, 2-(dimethylamino)ethyl acrylate, 2-(diethylamino)ethyl acrylate, 3-(dimethylamino)propyl acrylate, acrylic acid
Temperature	N-isopropylacrylamide
Ionic Concentration	Vinylimidazole or substituted versions

Future Work

The patent noted above provides a solution to sealing voids in a well. However, the triggerable gel may be limited in functionality. In current embodiments, a trigger is required to swell the gel, if that stimulus is removed from the system the gel will collapse to its original state, restoring flow through the voids. While the ability to turn the gel on and off certainly has applications, in the case of sealing voids, it may be beneficial to eliminate the off portion. Moving forward, routes to create hydrogels that will maintain its expanded phase when the trigger is removed will be accomplished with new compositions and monomers.

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